

# Transport Properties of Dichloromethane in Glassy Polymers. III. Drawn Atactic Polystyrene Films

V. VITTORIA\* and A. RUVOLO FILHO†

Dipartimento di Fisica, Università di Salerno, 84081 Baronissi (SA), Italy

## SYNOPSIS

Transport properties of dichloromethane vapor were measured in atactic polystyrene (aPS) samples, oriented by drawing at 95°C to different draw ratios (3 and 4.5) and analyzed after controlled aging times at different temperatures. The diffusional behavior is characterized by three zones, depending on vapor activity: In Zone I, at low activity, the diffusion coefficient is independent of vapor concentration; Zone II is characterized by concentration-dependent diffusion and by the appearance of non-Fickian sorption curves; and in Zone III, the strong interaction polymer-solvent induces disorientation of the samples. The diffusional behavior is very similar to that of undrawn aPS, and also the extrapolated parameters coincide, showing that in the case of amorphous polymers, the drawing does not influence the diffusion. The aging, both at room temperature and at 70°C, decreases the diffusion parameters and leads to the appearance of anomalous sorption curves. The sorption curve as a function of vapor activity does not show any difference for the fresh and aged at room temperature-oriented samples; furthermore, it coincides with that of aPS. At variance, the oriented samples aged at 70°C show a lower sorption at low activity. As in the case of aPS, the presence of ordered domains, impermeable to the penetrant at low activity, was suggested for the oriented samples. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

This paper is a part of a wider study on the transport properties of dichloromethane in glassy systems. At variance with rubbery systems, for which the relaxation times are generally shorter than the diffusion times and sorption curves following Fickian behavior are observed,<sup>1-3</sup> in glassy polymers, the sorption of organic vapors may involve time-dependent relaxation processes, and this, in turn, may determine an anomalous non-Fickian behavior.<sup>4-6</sup> Furthermore, the mode of transport is strongly influenced by the vapor activity, at constant temperature, and various regions of diffusional behavior can be observed.<sup>7</sup>

In previous papers,<sup>8,9</sup> we showed that the diffusional behavior of both atactic and syndiotactic polystyrene can be characterized by three zones, de-

pending on vapor activity: In Zone I, at low activity, the diffusion coefficient is independent of vapor concentration; Zone II is characterized by concentration-dependent diffusion; whereas in Zone III, at high activity, the strong interaction solvent-polymer can induce structural transformations.

The influence of aging time and temperature on the transport parameters and on the appearance of anomalous non-Fickian behavior was pointed out; it was found that the diffusion parameters of aged atactic and syndiotactic isomers do coincide. Furthermore, the possible presence of ordered domains, of such dimensions to be impermeable to the vapor at low activity, was suggested for the amorphous samples aged at 70°C, on the basis of sorption results.

The properties of glassy polymers are strongly influenced not only by the cooling conditions and the aging time, but also by molecular orientation, and great interest exists in the orientation introduced by drawing. For semicrystalline polymers, it was reported that the drawing dramatically reduces the transport parameters.<sup>10-12</sup> This effect is related

\* To whom correspondence should be addressed.

† Permanent address: Chemistry Department, Federal University of Sao Carlos, Cx Postal 676-13560 Sao Carlos (SP), Brasil.

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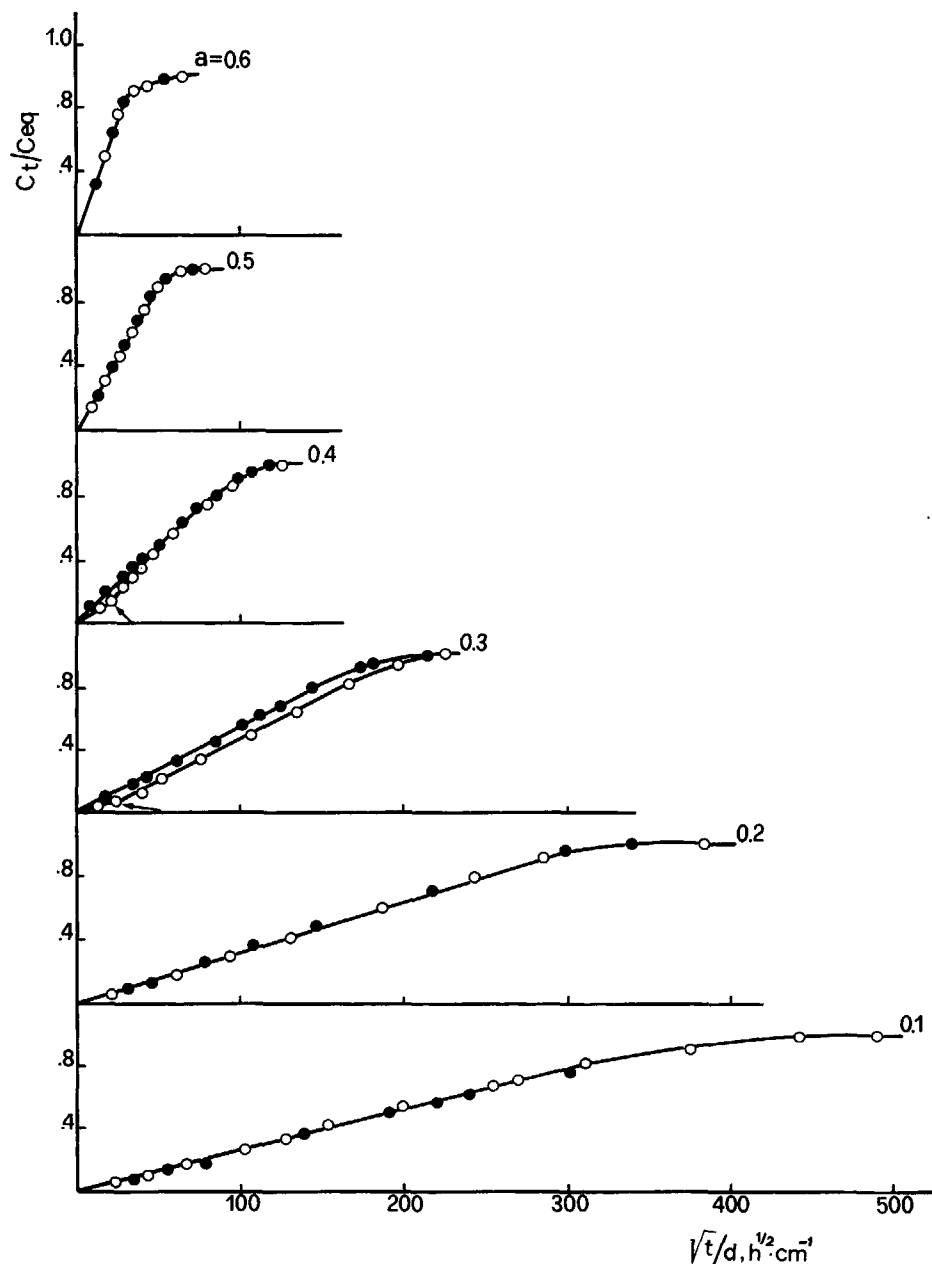
to the particular morphology of the drawn semi-crystalline samples<sup>13,14</sup>; it is interesting, therefore, to study the transport parameters of oriented systems in which the crystalline phase is absent. Moreover, if ordered domains, impermeable to vapor, are formed in the amorphous samples, their formation could be favored by molecular orientation introduced by drawing.

In this paper, we therefore analyze the transport properties of atactic polystyrene (aPS), oriented by drawing, with the aim (a) to determine the different

zones of diffusional behavior for different orientations and aging times; (b) to compare the diffusion parameters of oriented and unoriented samples; and (c) to point out if the orientation favors the formation of ordered domains.

## EXPERIMENTAL

Atactic polystyrene (aPS) powders of  $M_n = 74,300$  and  $M_w = 291,000$  were kindly supplied by RAPRA



**Figure 1** The reduced sorption curves,  $c_t/c_{eq}$ , as a function of  $\sqrt{t}/d$  ( $h^{1/2} \text{ cm}^{-1}$ ) for samples (●) 3F and (○) 4.5F at different activities.

(U.K.). Starting films were prepared by heating the powders above  $T_g$ , at 140°C, in a press, into a film shape of thickness 0.015–0.02 cm and quickly cooling to room temperature. The unoriented film was drawn at 95°C, using an air-heated Instron stretching machine, at an initial drawing rate of 1 cm/min; after drawing, the samples were cooled under stress to room temperature. The draw ratio was defined as  $\lambda = l/l_0$  ( $l_0$  is the initial length of the sample, and  $l$ , the length after drawing) and was measured by two ink marks printed on the sample.

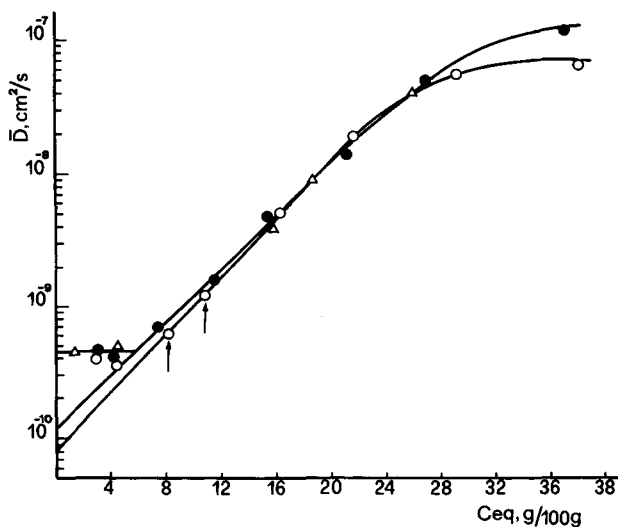
Samples drawn to  $\lambda = 3$  and 4.5 were analyzed as soon as prepared (samples 3F and 4.5F), after 2 months of aging at room temperature (samples 3R and 4.5R) and after two months of aging at 70°C (samples 3A70 and 4.5A70). Birefringence measurements showed that both samples are oriented.

Transport properties, sorption and diffusion, were measured by a microgravimetric method, using a quartz spring balance, having an extension of 2.2 cm/mg. The penetrant was  $\text{CH}_2\text{Cl}_2$  and the experiments were conducted at a temperature of 25°C. Sorption was measured as a function of vapor activity,  $a = p/p_T$ , where  $p$  is the actual pressure to which the sample was exposed, and  $p_T$ , the saturation pressure at the temperature of the experiment.

## RESULTS AND DISCUSSION

### Diffusion of Fresh Samples

In Figure 1 we report the reduced sorption curves, i.e.,  $c_t/c_{eq}$  as a function of  $\sqrt{t}/d$ , where  $c_t$  is the con-



**Figure 2** The logarithm of the mean diffusion coefficient  $\bar{D}$ , as a function of the vapor equilibrium concentration  $c_{eq}$ , for (●) sample 3F, (○) 4.5F, and fresh aPS (△).

**Table I** Diffusion Parameters  $D_{01}$  ( $\text{cm}^2/\text{s}$ ),  $D_{02}$  ( $\text{cm}^2/\text{s}$ ), and for All Analyzed Samples

Sample	$D_{01} \times 10^{10}$	$D_{02} \times 10^{11}$	
3F	4.5	12.2	23
4.5F	4.5	7.2	25
3R	4.8	5.5	30
4.5R	4.8	5.5	30
3A70	4.5	5.3	22
4.5A70	—	5.3	22
aPS <sup>a</sup>			
Fresh	4.6	12.2	23
Aged at room $T$	4.7	5.2	28
Aged at 70°C	4.6	5.3	22

<sup>a</sup> Data from Ref. 8.

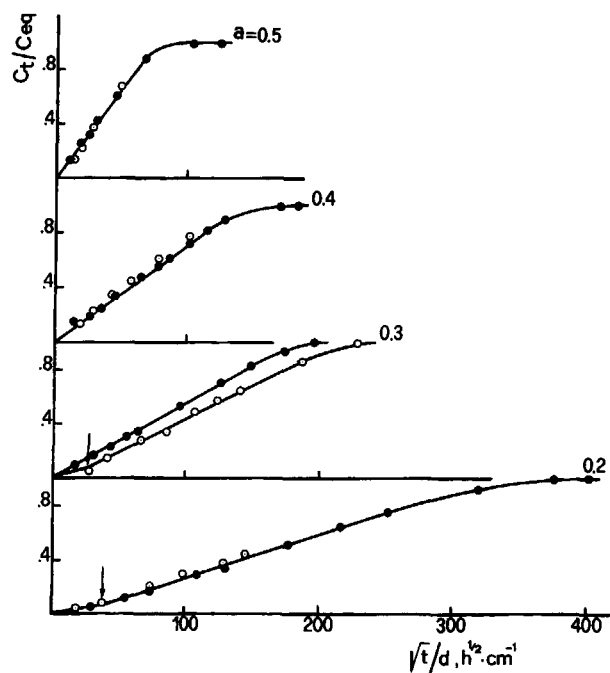
centration of vapor at time  $t$ ;  $c_{eq}$ , the equilibrium concentration; and  $d$ , the thickness (cm) of the sample, at different vapor activities, for the freshly drawn 3F and 4.5F samples. All the curves of sample 3F show a linear increase of concentration with square root of time, a downward curvature, and the equilibrium value of vapor concentration. This behavior is typical of Fickian sorption curves; it is therefore possible, at each vapor activity, to derive a mean diffusion coefficient<sup>1</sup> from the equation

$$c_t/c_{eq} = 4/d \sqrt{Dt/\pi} \quad (1)$$

The derived  $\bar{D}$  ( $\text{cm}^2/\text{s}$ ) values are mean values in the explored interval of concentration. To obtain the thermodynamic diffusion coefficient  $D_0$ , related to the free volume of the sample, it is necessary to find a correlation between  $\bar{D}$  and  $c_{eq}$ , allowing the extrapolation to  $c_{eq} = 0$ . Generally, this dependence is of the exponential form

$$D = D_0 \exp(\gamma c) \quad (2)$$

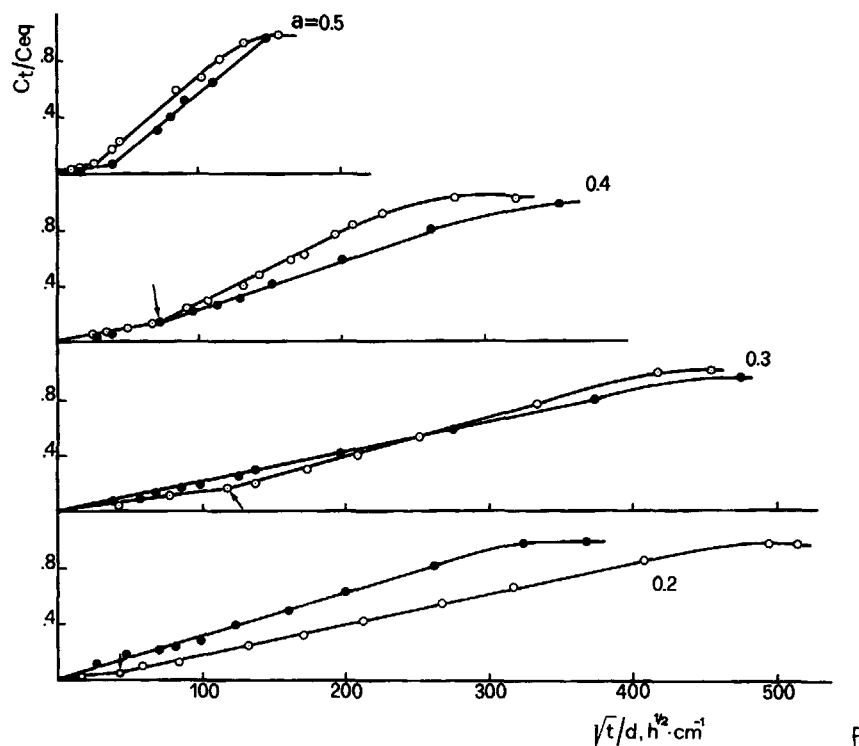
in which  $\gamma$  is the concentration coefficient, related to the fractional free volume and to the effectiveness with which the penetrant plasticizes the polymer.<sup>1-3</sup> Therefore, the logarithm of the  $\bar{D}$  values, derived from Figure 1 and eq. (1), are reported in Figure 2 as a function of  $c_{eq}$  for sample 3F. Also, in the figure, the experimental points of the undrawn fresh aPS sample of a previous paper<sup>8</sup> are reported. It is evident that the fresh drawn sample shows the same behavior as does the undrawn aPS. In particular, we observe three zones of behavior: At low activity, the diffusion values are independent of concentration (Zone I), and we derive a diffusion value  $D_{01}$ , which is the average of the experimental coefficients. At a critical activity, diffusion becomes de-



**Figure 3** The reduced sorption curves,  $c_t/c_{eq}$ , as a function of  $\sqrt{t}/d$  ( $h^{1/2} \text{ cm}^{-1}$ ), for samples (●) 3R and (○) 4.5R at different activities.

pendent on concentration (Zone II), and we can extrapolate to zero concentration a parameter  $D_{02}$  and a concentration coefficient  $\gamma$ . These parameters are reported in Table I, in which also the parameters for aPS of a previous paper<sup>8</sup> are reported. A curvature, after which diffusion becomes less dependent on concentration, defines Zone III of behavior, in which structural transformations are possible. We could not detect this zone in fresh undrawn aPS,<sup>8</sup> due to dissolution of the sample. In the present case of sample 3F, we do not observe the dissolution process, but a complete disorientation of the drawn sample, confirming that structural transformations are operative in this zone. From Table I we can observe that the diffusion parameters of fresh undrawn and drawn at  $\gamma = 3$  samples coincide.

The sorption curves of sample 4.5F show a Fickian behavior at all the activities, except at  $a = 0.3$  and  $0.4$ , where a slower increase of concentration is observed for short times; an arrow in the figure indicates the point after which a second linear increase of sorption with  $\sqrt{t}$  is observed. From this second part, a  $\bar{D}$  value for the corresponding activity was derived. The logarithm of the diffusion values, derived from the Fickian curves, are reported in Figure

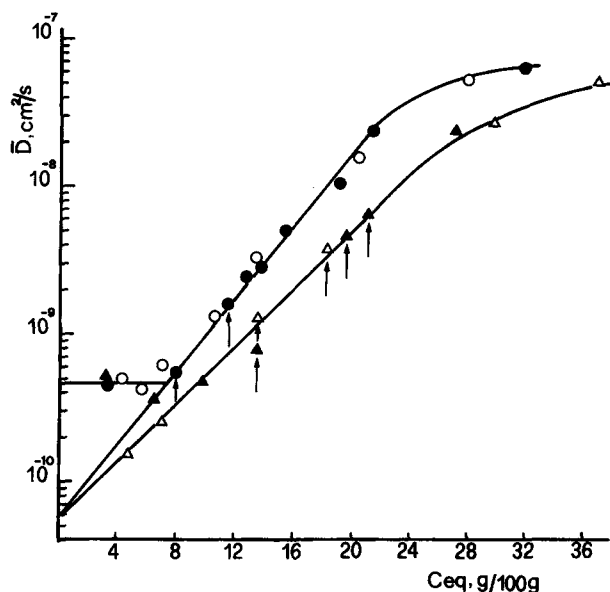


**Figure 4** The reduced sorption curves,  $c_t/c_{eq}$ , as a function of  $\sqrt{t}/d$  ( $h^{1/2} \text{ cm}^{-1}$ ), for samples (●) 3A70 and (○) 4.5A70 at different activities.

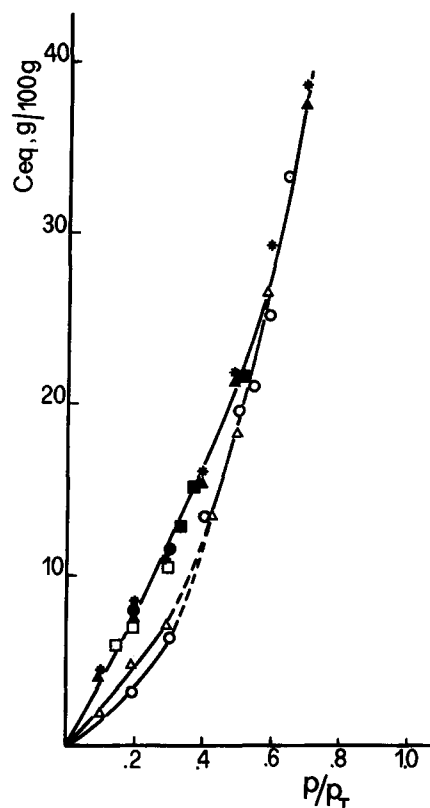
2 as a function of concentration; the two values of  $\bar{D}$ , obtained from the anomalous curves, are marked with an arrow in the figure. Also, the fresh 4.5F sample shows the three zones of different behavior. The diffusion parameters are reported in Table I. The  $\bar{D}_{02}$  parameter is lower and the  $\gamma$  coefficient higher than those of fresh undrawn and drawn to  $\lambda = 3$  samples.

### Diffusion of Aged Samples

In Figure 3 we report the reduced sorption curves as a function of  $\sqrt{t}/d$  for samples 3R and 4.5R, and that for samples 3A70 and 4.5A70 are shown in Figure 4 at different activities. It is evident that the aging strongly increases the anomalous behavior, particularly for samples aged at 70°C. The diffusion values, derived from the Fickian curves and from the second part of the anomalous curves (marked with an arrow), are reported in Figure 5 as a function of vapor concentration. The three zones of behavior are evident for all the samples, except for the 4.5A70 sample, for which the values at low activity fit the straight line of the second zone. The parameters derived from the different zones are reported in Table I. We notice that the diffusion parameters of the drawn samples coincide with those of the undrawn aPS. We can therefore conclude that, at variance with semicrystalline polymers, for which a dramatic



**Figure 5** The logarithm of the mean diffusion coefficient  $\bar{D}$  as a function of the vapor equilibrium concentration  $c_{eq}$ , for samples (●) 3R, (○) 4.5R, (▲) 3A70, and (△) 4.5A70.



**Figure 6** The equilibrium concentration of vapor as a function of activity  $a = p/p_T$ , for (\*) aPS and samples (●) 3F, (□) 4.5F, (■) 3R, (▲) 4.5R, (○) 3A70, and (△) 4.5A70.

decrease of diffusion parameters in drawn samples is observed, in the amorphous samples the drawing does not change the diffusional behavior.

### Sorption

In Figure 6 the equilibrium concentration of dichloromethane vapor is reported as a function of vapor activity for all the analyzed samples. Also, the curve of the undrawn aPS is reported for comparison.

In the limit of the experimental error, the sorption of the fresh and aged at room temperature samples fit the same curve as that of undrawn aPS. Therefore, at variance with semicrystalline polymers, the orientation in amorphous polymers changes neither the diffusion nor the sorption of dichloromethane vapor. Furthermore, the coincidence of sorption for undrawn and drawn samples could suggest that the orientation does not favor the formation of ordered domains; at least, if ordered domains are present in the drawn samples, they are not enough large to become impermeable to the penetrant. We suggested previously<sup>8</sup> that the ordered domains have to reach

a critical dimension to become impermeable to the vapor at low activity, and this condition was obtained for the undrawn samples annealed at 70°C. At low activity, the samples stored at 70°C show a lower sorption than do the samples aged at room temperature. At a critical activity, we observe a transition in the sorption curve, after which the samples show the same sorption as previously. Also, in this case, as for aPS, we can infer that the aging at 70°C promotes the formation of zones impermeable to the penetrant. In the present case, the transition range in the sorption curve is more extended than that of aPS. It extends up to activity  $a = 0.6$ , and this could be related to the dimensions of the ordered domains: i.e., the larger the dimensions, the higher the activity to become permeable. Also, in this case of drawn samples, we can observe that the anomalous sorption behavior is always present in the activity range in which the ordered zones are becoming permeable.

## CONCLUSIONS

The analysis of transport properties of dichloromethane in drawn aPS samples has shown that the diffusional behavior is not affected by the drawing. Also, in this case, it can be characterized by three zones, depending on vapor activity at constant temperature: At low activity, the diffusion coefficient is independent of vapor concentration and diffusion occurs mainly in a frozen system (Zone I). Zone II is characterized by diffusion parameters dependent on concentration, and the dependence was found to be of the exponential type, allowing the determination of a zero-concentration diffusion coefficient  $D_0$  and a concentration coefficient  $\gamma$ . In Zone III, the strong interaction can induce structural transformations; in the present case, the oriented samples lose the orientation.

The diffusion parameters of the drawn and aged samples coincide with those of the undrawn aPS samples. Only the sample drawn to  $\lambda = 4.5$  and analyzed as soon as possible (sample 4.5F) shows a diffusion coefficient lower than that of the undrawn aPS and intermediate between the fresh and the aged samples.

Also, the curve of sorption as a function of vapor activity is influenced neither by the aging at room temperature nor by the drawing. The storage at 70°C of the drawn samples produces a decrease of sorption at low activity; at higher activities, a transition in the sorption curve precedes a range in which all the analyzed samples show the same sorption. This leads to the suggestion that the aging at 70°C produces the formation of ordered domains, impermeable to the vapor at low activity. This effect is independent of drawing, having been observed also in undrawn aPS samples stored at 70°C.

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